SELF-BROADENING OF PRINCIPAL SERIES LINES OF RUBIDIUM AT HIGH NUMBER DENSITIES
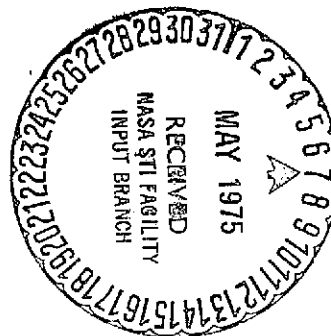
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16. Abstract

Self-broadening of principal series lines of rubidium has been studied using a steel absorption tube heated in an electric furnace. Line profiles were obtained with a grating spectrograph of high resolution in the temperature range 350-420°C corresponding to number densities of $18.6\text{-}119 \cdot 10^{15} \text{cm}^{-3}$. The half-widths of the lines disagree with classical impact calculations using dipole-dipole interaction but approach the asymptotic value of the quantum-mechanical polarization theory of Reinsberg.

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SELF-BROADENING OF PRINCIPAL SERIES LINES OF RUBIDIUM AT HIGH NUMBER DENSITIES

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I. Introduction

The resonance broadening of spectral lines of alkali metals has been the subject of numerous investigations for more than 40 years. However, these studies were usually restricted to the resonance lines [1-10] -- a major reason was the corrosiveness of alkali vapors at high temperatures and vapor densities. The desirable extension of these results to higher series terms has been made in [11-13]; in connection with the recent contribution of Schreiber et al [13], we now report measurements on self-broadening of principal series lines of rubidium. As in [13], /258 but unlike all previous studies of other authors, the number density was determined spectroscopically; this method avoids the use of the vapor-pressure curve, which is not always free of problems.

II. Theoretical Section

1. Spectroscopy of Absorption Lines

If a beam of light passes through a layer of gas of thickness ℓ with extinction coefficient κ_λ, the intensity of the background light $I_\lambda(0)$ and the transmitted intensity $I_\lambda(\ell)$ are connected by the relation

$$\kappa_\lambda = \frac{1}{l} \ln \frac{I_\lambda(0)}{I_\lambda(l)}.$$

(1)

If, for a given absorption line, $\ln [I_\lambda(0)/I_\lambda(\ell)]$ is plotted vs. the difference the wavelength and the center of the line, the resulting curve is that of the extinction coefficient; the

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*Numbers in the margin indicate pagination in the foreign text.

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width of this profile is the desired half-width. The extinction coefficient κ_0 in the center of the line and $\kappa_{1/2}$ at the half-width are found from (1) to be:

$$\kappa_0 = \frac{1}{l} \ln \frac{I_0}{I_{\min}} \quad \text{and} \quad \kappa_{\frac{1}{2}} = \frac{1}{l} \ln \frac{I_0}{I_{\frac{1}{2}}} \tag{1a}$$

with

$$\kappa_{\frac{1}{2}} = \kappa_0/2. \tag{1b}$$

The intensity at the half-width is then:

$$I_{\frac{1}{2}} = (I_0 \cdot I_{\min})^{\frac{1}{2}}; \tag{1c}$$

in other words, to determine the half-width, it is not necessary to plot the entire logarithmic profile; instead, it is enough to read off the entire width at intensity $I_{1/2}$. It is well-known that integration over the entire logarithmic profile of the absorption line yields:

$$\int_{-\infty}^{+\infty} \kappa_\lambda \, d\lambda = \frac{\pi e^2}{m_e c^2} \lambda^2 N f; \tag{2}$$

In this equation, e, m_e and c are the well-known physical constants, λ the central wavelength of the spectral line, N the number density of the absorbing level, and f the absorption oscillator strength From the experimental values of this integral, together with (1), it is easy to determine the number density of absorbing atoms, as long as the oscillator strength is known.

Along with this method of determining the half-width of absorption lines, indirect methods are frequently used in which a damping distribution is assumed for the profile of the

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extinction coefficient:

$$\kappa_\lambda = \frac{\pi e^2}{m_e c} N f \frac{\gamma}{\left(\frac{2\pi c}{\lambda_0^2}\right)^2 \Delta\lambda^2 + \left(\frac{\gamma}{2}\right)^2};$$ (3)

$\Delta\lambda$ is the separation from the center λ_0 of the line, and γ is the damping width (in angular-frequency units). The overall absorption obeys:

$$A = \int_{-\infty}^{+\infty} \left(1 - \frac{I_\lambda(l)}{I_\lambda(0)}\right) d\lambda;$$ (4)

for great optical depths τ_0 in the center of the line:

$$\tau_0 = \frac{\pi e^2 N f l}{m_e c} \frac{4}{\gamma}$$

(4), according to Ladenburg and Reiche [14] leads to the simple expression:

$$A = \frac{e\lambda_0}{(m_e c^3)^{\frac{1}{2}}} \left(\frac{\gamma f}{N}\right)^{\frac{1}{2}} N l^{\frac{1}{2}}.$$ (4a)

If the equivalent widths are plotted against number density, the result is a straight line, and it is easy to determine the damping width γ from the slope of this line.

Since this method can be applied only to strong absorption lines, it is impossible to make a comparison with measurements from the direct method (1).

2. Broadening of alkali principal series lines

A discussion [13] of competing causes of the broadening, using typical values for number densities and temperature, led to the conclusion that the measured line widths of rubidium lines are due entirely to interaction with rubidium atoms.

Weisskopf [15-17] assumed dipole-dipole interaction between the alkali atoms. The resulting interaction potential, together with the equations of collision damping theory (Lindholm [18]) eventually yield the damping constant:

$$\gamma_3 = \pi^2 \frac{e^2 fN}{m_e \omega_0};$$

(5)

In this equation, f is the oscillator strength of the transition generating the line, and ω_0 is its angular frequency. The validity of these equations is limited, however, by

$$\left(\frac{4\pi}{3} N\right)^{-\frac{1}{3}} \gg \rho_0,$$

(5a)

Here ρ_0 is the "Weisskopf" collision radius associated with phase disturbance 1:

$$\rho_0 = \left(\frac{4\pi C_3}{v}\right)^{\frac{1}{2}},$$

(5b)

where C_3 is the interaction constant of the elementary law: $\Delta\omega = 2\pi C_3/r^3$ and v is the relative velocity of the collision partner.

The assumption underlying the quantum-mechanical calculation of the interaction potential of identical particles, namely that the atomic dimensions are small in comparison with the distance between the colliding partners, according to Bates and Damgaard [19] resulted in the condition:

$$\frac{a_0}{\sqrt{2}} n^* [(5n^{*2} + 1 - 3l(l+1))]^{\frac{1}{2}} \ll \left(\frac{4\pi}{3} N\right)^{-\frac{1}{3}};$$

(6)

n* is the effective principal quantum number and ℓ the secondary quantum number.
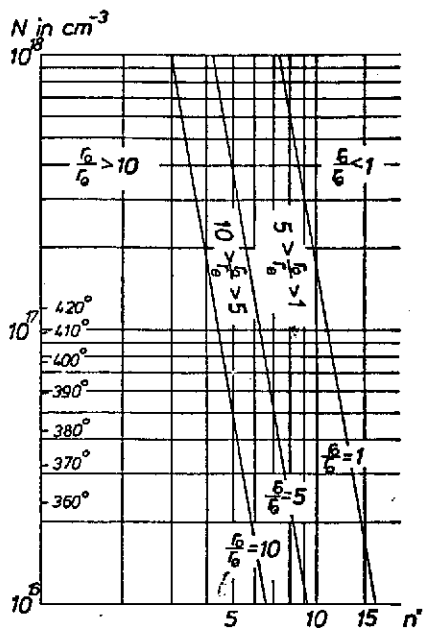
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Fig. 1. Comparison of average distance between two atoms r_0 with "atomic radius" of various excited states r_e according to Bates and Damgaard [19] (effective principal quantum number n^*). The ordinates show, together with the rubidium atomic densities, the associated temperatures (assuming saturated vapor). The measured values lie largely in the region $r_0/r_e < 1$.

Numerical calculations show that as in [13], condition (6) is not satisfied for high series terms and large number densities here either; Fig. 1 shows this situation.

Reinsberg's [20] quantum-mechanical calculations of the asymptotic collision cross section (Fermi) obtained the following limit for the damping width at the series limit:

$$\gamma_\infty = 5 \cdot 2^{\frac{1}{2}} \pi^{\frac{1}{2}} \left(\frac{\alpha e^2 \pi^3}{2h} \right)^{\frac{2}{5}} \left(\frac{kT}{\pi\mu} \right)^{\frac{3}{10}} N;$$

(7)

In this equation, μ is the reduced mass of the colliding particles, and α the polarizibility of the interfering atom (in this case, the rubidium atom)[1]

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[1] According to Sternheimer [21], the value used for the numerical relations is $\alpha = 49.1 \cdot 10^{-24} \text{cm}^3$.

III. Experimental Conditions

1. Absorption vessel and electrical furnace

The absorbing rubidium vapor was produced in an absorption tube made of a heat-resistant and a scale-resistance steel, the tube being heated in an evacuating electrical tube furnace to temperatures as high as 420°C. Details of the design can be seen in [13]. As opposed to [13], soft annealed copper rings provided with cutting edges were used to produce the high-temperature-resistant seal of the sapphire windows.

2. Optical arrangement

A xenon high-pressure lamp was again used to produce the background continuum. Quartz lenses focused the arc in the center of the absorption tube and then on to the slit of the spectrograph (3.4 m grating spectrograph, Ebert setup, 5.1 Å/mm in first order). To produce the intensity marks, an auxiliary beam path illuminated a step filter with fine transparency gradations. Because of the high light intensity of the xenon lamp, relatively insensitive and thus fine-grained Ilford N 30 plates were used to record the spectra and always gave Schlieren-free layers after hard development.

IV. Results

1. Spectra

The principal series lines of rubidium were recorded from the second series term ($5s^2S_{1/2} - 6p^2P_{1/2}$) at 4215 Å up to the series limit at 2967 Å. Generating the spectra in the interval of 350-420°C with an increment of 10°C proved to be a favorable procedure; at lower temperatures, the vapor densities, and thus the line widths, were so small that they could not be resolved. Higher temperatures resulted in complete absorption in the line profiles.

The measurements covered 32 lines of the principal series of rubidium with the transitions $5s^2S_{1/2} - np^2P_{1/2, 3/2}$ ($6 \leq n \leq 37$). Extending the measurement to still higher series terms would have required a further increase in vapor densities; however, this would make the lines so broad they could no longer be separated.

The resonance lines could not be measured directly, since, because of the high oscillator strength of these transitions, analyzable absorption depths were not obtained unless the number densities were such that the line width was close to the 80 mÅ apparatus width. Analysis by the indirect method from the total absorption (4a) was omitted in this case, since the required determination of vapor density from total absorption of higher series terms could not be carried out because the absorption depth was too small.

2. Analysis of Spectra

The intensities were measured with a microphotometer; the readings were converted to intensity units via optical density curves.

a) Half-widths. In accordance with (1), the half-widths of the lines are the half-widths of the logarithmic intensity profiles; (1c) was used for a quick determination. The measurement yielded half-widths between 150 mÅ to 600 mÅ; at half-widths less than 200 mÅ, the apparatus width was taken into account. For the transitions $5s^2S_{1/2} - np^2P_{1/2, 3/2}$ ($5 \leq n \leq 10$), the doublet components could be resolved and measured separately. /263 From the transition $5s^2S_{1/2} - 11p^2P_{1/2, 3/2}$ on, this was no longer possible; however, the separation of the components was negligibly small in comparison to the measured half-widths beyond about n = 15, so that the nonresolvability of the components caused falsification in the results only in the intervening region.
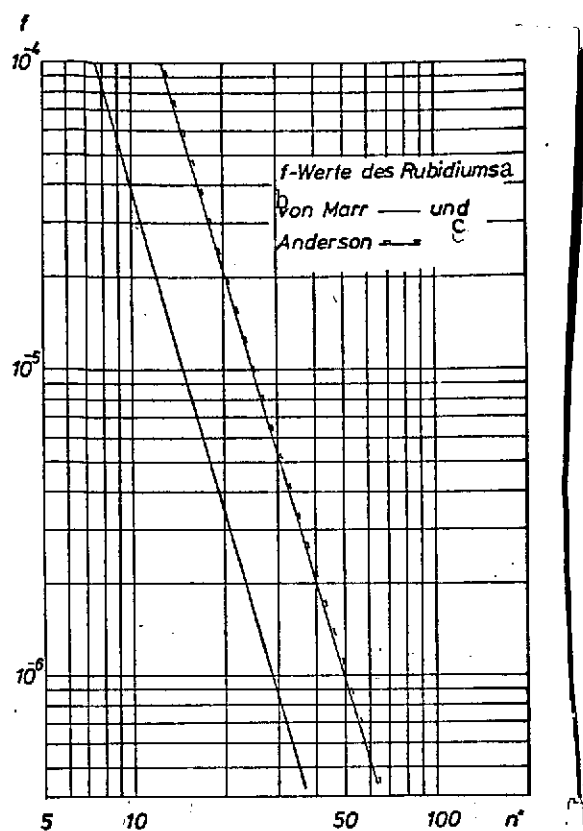
f-Werte des Rubidiums a
von Marr —— und c
Anderson ⊷⊷

Fig. 2. Absorption oscillator strengths of principal series lines of rubidium as a function of effective principal quantum number n* according to Marr and Creek [22] or Anderson and Zilitis [23].

Key: a. f-values of rubidium
     b. of
     c. and

b) Number densities. Rubidium number densities were determined from different lines of a single spectrum by integration over the logarithmic absorption curve as in (2); the accuracy of this procedure is essentially determined by the information on oscillator strengths. Because of the superior /264 agreement with the vapor pressure curve [24], the oscillator strengths of Marr and Creek [22] were again used, as in [13]. Fig. 2 illustrates the uncertainty which still exists in the data on oscillator strengths for the principal series lines of rubidium, by comparing these values with those given by Anderson and Zilitis [23].

c) Half-widths (determined by (4a) from total absorption. In order to discover whether the direct determination of half-width from the logarithmic absorption curves using (1) and (1c) was equivalent to obtaining values by (4a) from total absorption, both methods were applied to the line $5s^2S_{1/2} - 21p^2P_{1/2, 3/2}$ for various number densities. The value of $2\Delta\lambda_{1/2}/N$ (obtained from direct measurement ($\Delta\lambda_{1/2}$ = half the half-width in wavelength units) was $0.45 \cdot 10^{-25} cm^{-4}$, and this was

2.1 times greater than the indirectly determined value of 0.2 $\cdot 21 \cdot 10^{-25} \mathrm{cm}^{-4}$. These discrepancies can be ascribed partly to the violation of (4a) $(\tau_0 \gtrsim 10)$; in this case, the optical depth in the center of the line was only 1.5. The influence of neglecting the term $(\gamma/2)^2$ in the dispersion denominator on the equivalent widths was investigated; the resulting differences of 40% gave damping constants smaller by a factor of 1.4 than the values determined by the direct method. Remaining discrepancies can be explained by errors in measurement and by profiles deviating from the dispersion type.

3. Discussion of Errors in Measurement

In the photographic-photometric method of measurement, the errors in the half-widths are probably not less than 15%. When the number density was determined, there were deviations of 10% from the mean value. Thus, the given values for $2\Delta\lambda_{1/2}/N$ or γ/N must be anticipated to have uncertainties of 25%. For lines with large half-widths, this value is probably not exceeded, while effects of the apparatus must be taken into account in the case of narrow lines. If the spacing between the doublet components is comparable with the half-width, this will also result in systematic discrepancies.

4. Results

In Fig. 3, the half-width of the rubidium line $5s\,^2S_{1/2} - 22\,p\,^2P_{1/2, 3/2}$ is plotted against number densities; in Table 1, the (entire) half-widths (in $\overset{\circ}{A}$ and in angular-frequency units), expressed in terms of the number density, are listed together with the oscillator strengths of the lines. Fig. 4 shows the linear dependence of the half-width on the oscillator strength for the lines $15 \lesssim n \lesssim 28$ at a number density of $59 \cdot 10^{15} \mathrm{cm}^{-3}$; for other densities, the relations can also be represented by straight lines. Consequently:

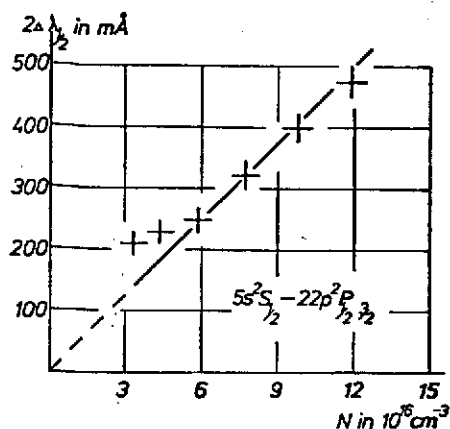$$\gamma = \mathrm{const} \cdot fN; \qquad (8)$$

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Fig. 3. (Entire) Half-width
of rubidium line
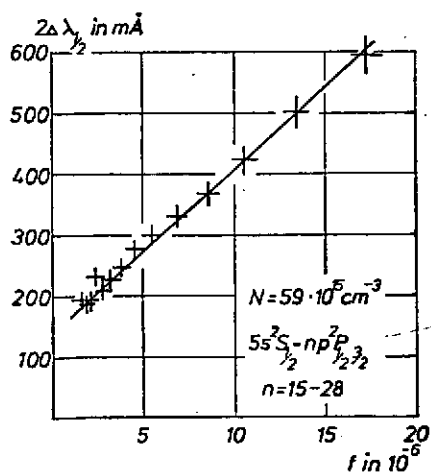$5s^2S_{1/2} - 22p^2P_{1/2, 3/2}$ vs.
number density of rubidium
atoms.

Fig. 4. (Entire) Half-width
of rubidium lines
$5s^2S_{1/2} - np^2P_{1/2, 3/2}(15 \leq n \leq 28)$
at number density
$59 \cdot 10^{15}cm^{-3}$ vs. oscillator
strength according to Marr and
Creek [22].

differs from the result (5),
obtained from calculations of
dipole-dipole interaction and
from collision damping theory,
by the value of the constant,
which is larger in this case
by a factor of about 10^5.
Fig. 5 shows the damping
constant relative to rubidium
density as a function of the
principal quantum number of
the upper level of the line,
and Fig. 6 shows the quotient /268
$2\Delta\lambda_{1/2}/N$ as a function of
oscillator strength for the
rubidium lines discussed in
this work and the potassium
lines from [13]; the propor-
tionality to oscillator
strength is again noteworthy.
As Fig. 5 implies, the half-
widths converge to a finite
limit when the series limit is
approached, which is consistent
with the predictions of
Reinsberg's theory [20]. The
width measured for the
$5s^2S_{1/2} - 35p^2P_{1/2, 3/2}$ line
relative to number density
was $\lambda/N = 3.2 \cdot 10^{-6}cm^3sec^{-1}$,
while the value calculated from
the asymptotic collision cross
section by (7) was

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TABLE 1. MEASURED HALF-WIDTHS VS. NUMBER DENSITY

Column (1) contains the transition, (2) the wavelength of the line and (3) the absorption oscillator strength according to Marr and Creek

(1) Transitions $5s\,^2S_{1/2}$	(2) λ_0 in Å	(3) f	(4) $\dfrac{2\Delta\lambda_{\frac{1}{2}}}{N}$ cm^4	(5) $\dfrac{\gamma}{N}$ cm^3 sec^{-1}
$-7p\,^2P_{1/2}$	3591	$0.8 \cdot 10^{-3}$	$15.3 \cdot 10^{-26}$	$22 \cdot 10^{-6}$
$-7p\,^2P_{3/2}$	3587	$1.6 \cdot 10^{-3}$	23.8	35
$-8p\,^2P_{1/2}$	3350	$2.4 \cdot 10^{-4}$	8.7	14
$-8p\,^2P_{3/2}$	3348	$4.8 \cdot 10^{-4}$	14.2	24
$-9p\,^2P_{1/2}$	3229	$1.0 \cdot 10^{-4}$	6.7	13
$-9p\,^2P_{3/2}$	3227	$2.0 \cdot 10^{-4}$	12.7	23
$-10p\,^2P_{1/2}$	3158	$4.8 \cdot 10^{-5}$	6.4	12
$-10p\,^2P_{3/2}$	3157	$9.6 \cdot 10^{-5}$	10.3	19.5
$-15p\,^2P_{1/2,3/2}$	3031	$1.7 \cdot 10^{-5}$	9.3	18.8
$-16p\,^2P_{1/2,3/2}$	3022	$1.35 \cdot 10^{-5}$	8.7	17.5
$-17p\,^2P_{1/2,3/2}$	3014	$1.04 \cdot 10^{-5}$	7.5	15.7
$-18p\,^2P_{1/2,3/2}$	3008	$8.25 \cdot 10^{-6}$	7.0	14.6
$-19p\,^2P_{1/2,3/2}$	3003	$6.69 \cdot 10^{-6}$	5.8	11.3
$-20p\,^2P_{1/2,3/2}$	2999	$5.48 \cdot 10^{-6}$	4.8	10.1
$-21p\,^2P_{1/2,3/2}$	2996	$4.57 \cdot 10^{-6}$	4.5	9.3
$-22p\,^2P_{1/2,3/2}$	2993	$3.85 \cdot 10^{-6}$	4.0	8.5
$-23p\,^2P_{1/2,3/2}$	2990	$3.28 \cdot 10^{-6}$	3.5	7.3
$-24p\,^2P_{1/2,3/2}$	2988	$2.8 \cdot 10^{-6}$	3.0	6.5
$-25p\,^2P_{1/2,3/2}$	2986	$2.4 \cdot 10^{-6}$	2.7	5.8
$-26p\,^2P_{1/2,3/2}$	2985	$2.0 \cdot 10^{-6}$	2.3	5.1
$-27p\,^2P_{1/2,3/2}$	2983	$1.8 \cdot 10^{-6}$	2.1	4.7
$-28p\,^2P_{1/2,3/2}$	2982	$1.5 \cdot 10^{-6}$	2.0	4.5
$-29p\,^2P_{1/2,3/2}$	2981	$1.35 \cdot 10^{-6}$	1.9	4.3
$-30p\,^2P_{1/2,3/2}$	2980	$1.2 \cdot 10^{-6}$	1.8	4.0
$-31p\,^2P_{1/2,3/2}$	2979	$1.1 \cdot 10^{-6}$	1.9	4.3
$-32p\,^2P_{1/2,3/2}$	2978	$9.4 \cdot 10^{-7}$	1.7	3.8
$-33p\,^2P_{1/2,3/2}$	2977	$8.5 \cdot 10^{-7}$	1.7	3.7
$-34p\,^2P_{1/2,3/2}$	2977	$7.6 \cdot 10^{-7}$	1.6	3.3
$-35p\,^2P_{1/2,3/2}$	2976	$6.8 \cdot 10^{-7}$	1.6	3.2

$\gamma_\infty/N = 0.25 \cdot 10^{-6}$ cm^{3}sec^{-1}. However, it is dubious whether this limit has been reached by n = 35.

Concluding Remarks

In order-of-magnitude terms, the line widths reported in this work for the principal series lines of rubidium can be interpreted by the quantum-mechanical polarization equations for the equation process given by Reinsberg. However, it is desirable that the measurements be extended to cover a wider
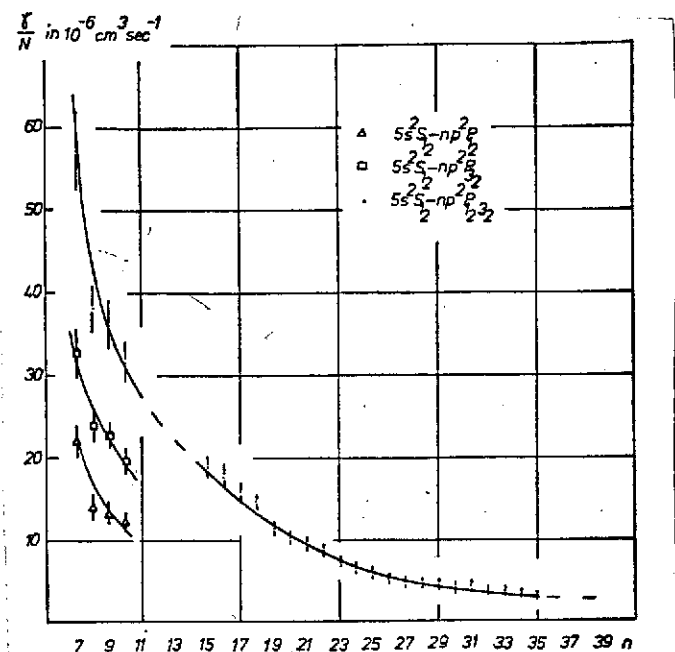
Fig. 5. Damping constant of principal series line of rubidium divided by number density as a function of principal quantum number. According to Reinsberg [20], γ/N converges to a limit for large n.
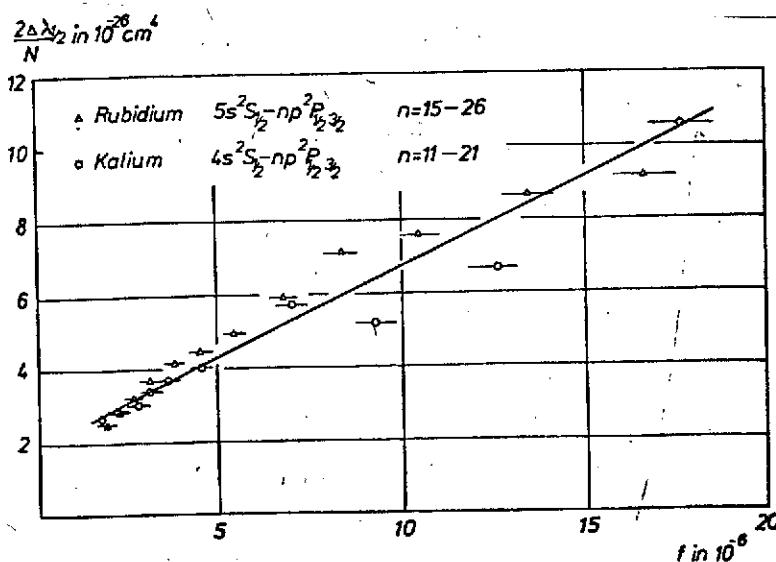

Fig. 6. (Entire) Half-width (in wavelength units) of rubidium and potassium [13] lines, divided by number density, in relation to absorption oscillator strengths given by Marr and Creek [22]; surprisingly, the dependence is the same for the potassium and rubidium lines.

range of number densities, first so that the hypotheses of collision theory would be satisfied better, and second to study the interaction at higher vapor densities up to the transition to chemical bonding. In order to achieve equal absorption depths at lower densities, the light beam must pass through the absorption tube many times and interferometric techniques must be employed. The length of the absorption cell should be reduced for direct measurements of line widths at high vapor densities.

Further studies of this type are in progress; they will be reported once they are concluded.

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